



# TechData Sheet



Naval Facilities Engineering Service Center  
Port Hueneme, California 93043-4370

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**February 1999**

*Advanced Fuel Hydrocarbon Remediation National Test Location*

## *Natural Attenuation of MTBE in an Anaerobic Groundwater Plume*

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### Introduction

Methyl tertiary butyl ether (MTBE) is a compound commonly added to petroleum fuels as an oxygenate or octane enhancer often at concentrations above 10 percent by volume. MTBE is currently in 70 percent of the gasoline used in the United States. Due to its high water solubility, it is commonly a significant groundwater contaminant at sites affected by fuel spills. Once in the groundwater, MTBE migrates due to predominate water flow with little retardation, but may be removed by volatilization or degradation under the right conditions. A natural attenuation study is being conducted at Port Hueneme, California, to gather information on the behavior and degradation of MTBE under conditions common to fuel contaminated sites, namely under oxygen depleted conditions, resulting from microbial degradation of other petroleum hydrocarbons.

The study is using a solution of perdeuterated MTBE ( $^2\text{H}_{12}$ -MTBE) as a tracer to measure the natural attenuation of MTBE in an existing plume. Since deuterated molecules have a slightly higher molecular weight than the commonly occurring ( $^1\text{H}_{12}$ -MTBE) molecules, the  $^2\text{H}_{12}$ -MTBE tracer and its degradation

products can be distinguished from existing MTBE using a gas chromatograph with a mass selective detector.

### Bioremediation

Intrinsic bioremediation refers to the natural attenuation of contaminated soil and groundwater sites due to natural biological processes, as opposed to abiotic chemical and physical processes. Bioremediation by indigenous microorganisms typically occurs at all contaminated sites, but to varying degrees of effectiveness and lengths of time. Biological processes may reduce the potential risk posed by site contaminants in two ways:

- The contaminant may be converted to a less toxic form through destructive processes or transformation; and
- Potential exposure levels may be reduced by lowering of concentration levels.

In order for bioremediation to proceed, microorganisms must meet certain nutritional and energy requirements to grow and multiply.

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Microorganisms obtain energy by transferring electrons from electron donors, such as the organic contaminant, to compounds that accept electrons (e.g., oxygen). At many petroleum fuel spill sites, the regulated fuel hydrocarbon compounds benzene, toluene, ethyl benzene, and xylene (the BTEX compounds) and polycyclic aromatic hydrocarbons components may naturally degrade through microbial activity and ultimately produce non-toxic end products (e.g., carbon dioxide, water, and/or methane). A key component of the degradation process is transfer of electrons directly to inorganic compounds (e.g., nitrate) that act as terminal electron acceptors. The following electron acceptors are listed in decreasing order of energy production per organic molecule:

- oxygen ( $O_2$ )
- nitrate ( $NO_3^-$ )
- ferric (III) iron ( $Fe^{3+}$ )
- sulfate ( $SO_4^{2-}$ )
- carbon dioxide ( $CO_2$ )

In order for contaminant degradation to be sustained, both carbon sources and electron acceptors must be present.

While BTEX contaminants tend to biodegrade with relative ease and polycyclic aromatic hydrocarbons with a lesser degree of ease, MTBE is more resistant to biological degradation. MTBE plumes typically extend downgradient from gasoline spills (Figure 1). The presence of fuel hydrocarbons in ground water causes a reduction of dissolved oxygen and other electron acceptors and may be a reason for MTBE's relatively recalcitrant nature when compared to most other gasoline components. For site remediation assessment with respect to natural attenuation of MTBE, characterization should include evaluation of the availability of nutrients, type and concentration level of electron donors, and acceptors, and the presence of metabolic by-products.

### Natural Attenuation Study Site

The study site is an existing fuel hydrocarbon plume

that resulted from a 1984 fuel release at the Navy Exchange (NEX) service station at Port Hueneme, California. The plume occurs in a shallow semi-perched water table aquifer. Constituents of concern are the BTEX compounds and MTBE. The plume can be divided into two zones:

- one in which residual non-aqueous phase liquids still persist
- one in which contaminants (primarily MTBE) are in the dissolved phase only (Figure 1)

The tracer study is also being conducted within the dissolved contaminant plume. Based on the length of the plume and the amount of time since the spill, the calculated groundwater velocity is 0.74-foot per day. The existing MTBE plume is approximately 4,000 feet long and 540 feet wide. The tracer was injected approximately 800 feet directly downgradient from the original spill location (Figure 1). The tracer will be transported from a zone of dissolved MTBE and BTEX contamination to a zone with dissolved MTBE as the main contaminant of concern during the course of the study.

### Assessing Downgradient Aquifer Characteristics

The chemical and soil characteristics of the aquifer downgradient of the tracer injection location was assessed prior to the study and will continue to be assessed throughout the experiment. Knowing these parameters makes it easier to evaluate the tracer fate and migration path in relation to specific chemical or hydrogeologic zones it passes through. Groundwater samples are being collected and analyzed for the water parameters listed in Table 1. Hydraulic conductivity is being measured using in-situ slug tests.

### Description of Tracer Test

The tracer solution contained  $^2H_{12}$ -MTBE, sodium bromide (NaBr), and fluorescein (Figure 2). Hydrogen atoms occur in nature with masses of one ( $^1H$ ) and two ( $^2H$ ); these molecules are non-

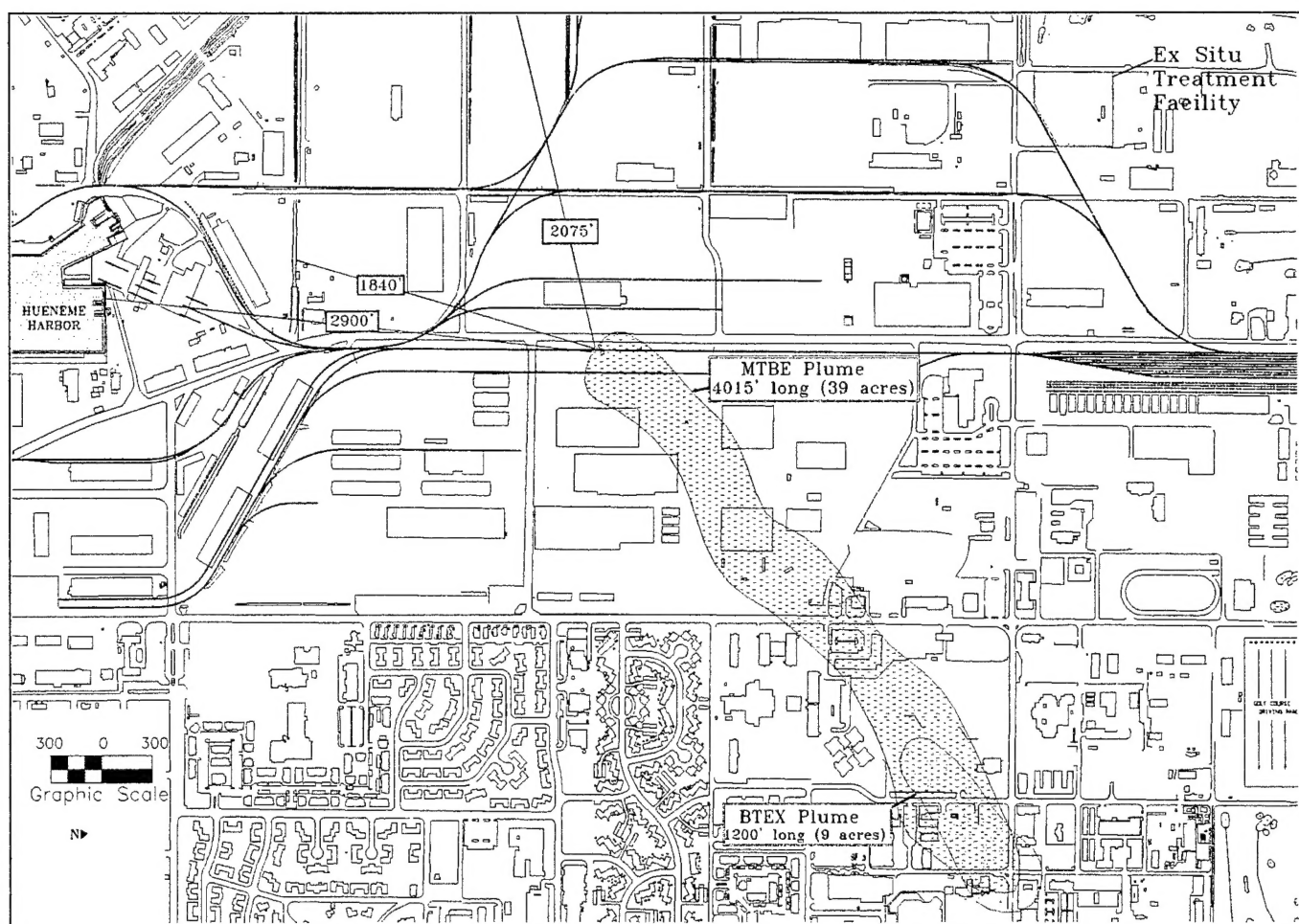


Figure 1. Fuel hydrocarbon plume.

Table 1. Ground Water Quality Parameters

Water Quality Parameter
Dissolved oxygen
pH
Redox potential (Eh)
Nitrate
Sulfate
Iron (II)*
Methane*
Organics (BTEX and MTBE)*
Hydrogen*

\*On selected samples

radioactive unlike produced hydrogen tritium with a mass of three ( $^3\text{H}$ ). The  $^2\text{H}_{12}$ -MTBE is a 98 percent isotropic purity custom chemical. The target concentration of  $^2\text{H}_{12}$ -MTBE within the tracer plume

was 1 mg/L. Bromide, whose transport is similar to MTBE, was added in concentrations of 500 mg/L. The bromide was added as a conservative (non-volatile, non-biodegradable) tracer, with which the remaining mass of  $^2\text{H}_{12}$ -MTBE can be compared. The

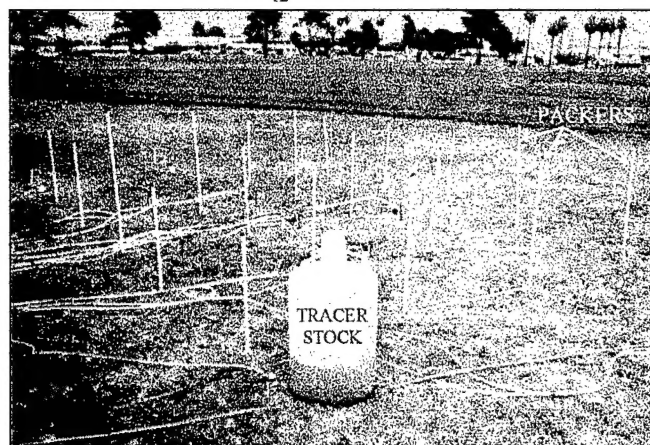


Figure 2. Tracer stock solution with injection and extraction wells pattern.

fluorescein dye was added to provide an indication that  $^2\text{H}_{12}$ -MTBE and NaBr might be present in the groundwater.

The injection arrangement consisted of ten groundwater "extraction" wells surrounding five central "injection" wells (Figure 3). These wells were within the sampling grid for the initial tracer plume characterization. Since it is imperative that the tracer makeup water be representative of aquifer conditions (e.g., dissolved oxygen, redox potential), the actual groundwater was used to "mix" the tracer solution *in-situ*. Groundwater was extracted from the ten extraction wells and blended at the five injection wells with a low flow feed of the tracer stock solution. The mixed groundwater and tracer solution were maintained in a reduced oxygen condition. The solution was then injected into the five injection wells. Peristaltic pumps were used for both the extraction and injection processes. The extent of the initial tracer plume with  $^2\text{H}_{12}$ -MTBE was 5m in diameter with a thickness of approximately 2.5 meters.

Groundwater samples were collected immediately after the tracer injection was completed to define the extent and assess the  $^2\text{H}_{12}$ -MTBE mass of the initial plume. The distribution and concentration of the  $^2\text{H}_{12}$ -MTBE and bromide within the MTBE plume will be characterized using temporary sampling points after four months, eight months, and two years of plume migration. Sample collection locations at the one year and two year events will correspond to a 9 by 9 meter sample grid. At each grid point, samples will be collected at a minimum of five discrete depths to determine the vertical distribution of the tracer plume. This will result in the collection of approximately 400 samples for each sampling event. Results of the bromide analysis and/or presence of fluorescein will be used to further refine the sampling density within the plume. If necessary, additional samples will be collected before performing the mass balance on the  $^2\text{H}_{12}$ -MTBE.

After 1 year and 2 years of plume migration, the mass of  $^2\text{H}_{12}$ -MTBE remaining in the plume will be

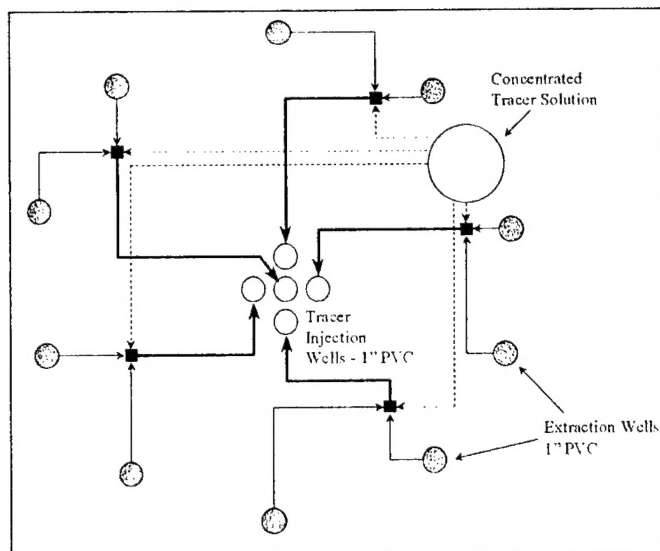


Figure 3. Injection and extraction wells configuration.

determined by integrating the groundwater concentration within the mapped plume. This value will be compared to the initial mass calculation and will offer the first assessment of  $^2\text{H}_{12}$ -MTBE degradation. The distribution of  $^2\text{H}_{12}$ -MTBE will be compared to that of the conservative bromide tracer in the groundwater. The same dispersive forces should have acted upon the two compounds; thus any decrease in concentration of the  $^2\text{H}_{12}$ -MTBE relative to the bromide should be attributable to degradation. While the  $^2\text{H}_{12}$ -MTBE and bromide tracers will undergo some dilution due to dispersion, dilution of the  $^1\text{H}_{12}$ -MTBE within the tracer plume will be minimal since the  $^1\text{H}_{12}$ -MTBE plume is much more extensive than the tracer plume. Therefore, a decrease in concentration of the total  $^1\text{H}_{12}$ -MTBE concentration within the tracer plume may also be evidence of MTBE degradation. Lastly, the appearance of  $^2\text{H}_{12}$ -labeled daughter products, such as tert-butyl alcohol (TBA), will indicate that biodegradation is occurring.

### Numerical Modeling

To better understand the relative importance of advection/dispersion and degradation to the migration of MTBE, a numerical model of the groundwater flow at the study site will be developed. The Department of Defense Groundwater Modeling System (GMS), which incorporates MODFLOW, MODPATH, and

MT3D, will be used for this purpose. Hydraulic conductivity data from existing cores and samples collected from the study site will be used along with measured hydraulic gradient data to model the aquifer's hydrologic properties. Concentration data for  $^2\text{H}_{12}$ -MTBE and sodium bromide collected over the course of the study will provide parameters for dispersion and degradation calculations.

### Use of Information

The data will be evaluated as discussed above in the description of the tracer test. The tracer test will yield quantitative information on the fate of MTBE during

migration under reducing conditions in the presence of other fuel hydrocarbons. This information will help assess the role of natural attenuation as a plume management strategy for MTBE. Numerical model data will provide a means to transfer information learned at this site to other Department of Defense and Navy sites where MTBE contamination is present.

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